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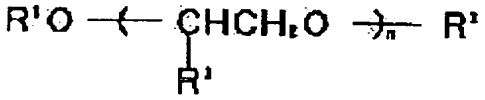
(54) GRIGNARD REAGENT

(57)Abstract:

PURPOSE: To obtain the subject reagent containing a specific ether as a solvent, capable of dissolving a halogenated magnesium complex produced as a byproduct in a coupling reaction and separating and purifying the product easily even in the case that the product is easily decomposed by water.

CONSTITUTION: This Grignard reagent of R4MgX (R4 is a 2-12C alkyl, an alkenyl, a 2-6C alkynyl, a 7-16C aralkyl, a 4-8C cycloalkyl or a 6-10C aryl; X is a halogen) comprises a polyalkyleneglycol dialkyl ether of the formula [R1, R2 are each a 1-8C alkyl; R3 is H or methyl; n is 1-6] (e.g. diethyleneglycol diethyl ether) as a solvent. Furthermore, it is preferable to add a hydrocarbon- based solvent such as n-hexane, cyclohexane, n-heptane, n-octane, n-decane, n-undecane, n-dodecane, benzene, toluene and xylene upon or after the preparation of the reagent.



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[Title of Invention]

Grignard reagent

[Abstract]

[Constitution] Grignard reagent of which the solvent is polyalkyleneglycoldialkylether expressed by the general formula [1]
[Chem. 1]

$$R^1O-\left(-\underset{\underset{R^3}{|}}{CHCH_2O}-\right)_n-R^2 \qquad (1)$$

(R^1, R^2 · alkyl group of carbon number 1 ~ 8, R^3 : hydrogen atom or methyl group, n : an integer 1 ~ 6).
[Effect] When the Grignard reagent of the present invention of which the solvent is polyalkyleneglycoldialkylether is used, the magnesium halide complex generated as the by-product of coupling reaction between the Grignard reagent and the other compound is dissolved, and even in case the product tends to be hydrolyzed by water, the product can be easily separated and purified by distillation, etc. without after-treatment with water.

[Claims]

[Claim 1] Grignard reagent, of which the solvent is polyalkyleneglycoldialkylether expressed by the general formula [1]
[Chem. 1]

$$R^1O-\left(-\underset{\underset{R^3}{|}}{CHCH_2O}-\right)_n-R^2 \qquad (1)$$

(in the formula, R^1, R^2 are alkyl groups of carbon number 1 ~ 8 and can be identical or different, R^3 is a hydrogen atom or a methyl group, and n is an integer 1 ~ 6), and which is expressed by the general formula [2]
[Chem. 2]

$$R^4MgX \qquad [2]$$

(in the formula, R^4 is an alkyl group of carbon number 2 ~ 12, alkenyl group of carbon number 2 ~ 12, alkynyl group of carbon number 2 ~ 6, aralkyl group of carbon number 7 ~

16, cycloalkyl group of carbon number 4 ~ 8, or aryl group of carbon number 6 ~ 10, and X shows a halogen atom)

[Claim 2] Grignard reagent according to the claim 1 featured in that hydrocarbon base solvent, which is n-hexane, cyclohexane, n-heptane, n-octane, n-decane, n-undecane, n-dodecane, benzene, toluene, or xylene, is added during or after its preparation.

[Detailed Description of the Invention]

[0001]

[Area of application in industry] The present invention relates to Grignard reagent of which the solvent is polyalkyleneglycoldialkylether.

[0002]

[Conventional technology] In the past Grignard reagent was prepared by using chain ether such as diethylether, dibutylether, etc. as the solvent, and recently it has been prepared by using cyclic ether such as tetrahydrofuran (THF), etc. as the solvent.

[0003]

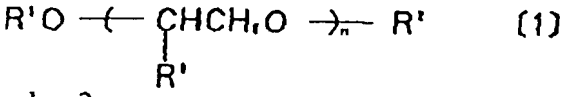
[Problems to be solved by the invention] For example, in the case of Grignard reagent of which the solvent is tetrahydrofuran, the magnesium chloride complex generated as the by-product of coupling reaction between the Grignard reagent and the other compound is not dissolved, and this complex is deposited as crystals or precipitate. Consequently, the problem is that the product cannot be separated and purified by such means as distillation, etc. without the preceding process to remove the deposited complex by such method as filtration, etc.. Although the complex can be removed out of the system by dissolving the deposited complex in water, this method cannot be used if the product tends to be hydrolyzed by water.

[0004]

[Method to solve the problems] Accordingly, the present inventors carried out intensive studies and found that, if a Grignard reagent is prepared by using a specific polyalkyleneglycoldialkylether as the solvent, the magnesium halide complex generated as the by-product of the subsequent coupling reaction can be dissolved, and as a result, even in case the product is easily hydrolyzed with water, the product can be separated and purified by distillation, etc. without after-treatment with water, and thus completed the present invention.

[0005] The present invention is a Grignard reagent, of which the solvent is polyalkyleneglycoldialkylether expressed by the general formula [1]

[Chem. 3]

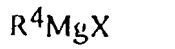


(1)

(in the formula, R^1, R^2 are alkyl groups of carbon number 1 ~ 8 and can be identical or different, R^3 is a hydrogen atom or a methyl group, and n is an integer 1 ~ 6), and which is expressed by the general formula [2]

[0006]

[Chem 4]



[2]

(in the formula, R^4 is an alkyl group of carbon number 2 ~ 12, alkenyl group of carbon number 2 ~ 12, alkynyl group of carbon number 2 ~ 6, aralkyl group of carbon number 7 ~ 16, cycloalkyl group of carbon number 4 ~ 8, or aryl group of carbon number 6 ~ 10, and X shows a halogen atom).

[0007] Furthermore, during or after the preparation of the Grignard reagent of the present invention, hydrocarbon base solvent such as n-hexane, cyclohexane, n-heptane, n-octane, n-decane, n-undecane, n-dodecane, benzene, toluene, xylene, etc. can be added. When these hydrocarbon base solvent is added in advance, the yield of Grignard reagent is increased drastically in the case of halides such as allyl chloride, benzyl chloride, etc.. Also, if the hydrocarbon base solvent is added before or after the preparation of Grignard reagent, after the coupling reaction between the Grignard reagent and the other compound, the reaction product can be liquefied (dissolved) if the product is solid at room temperature, prior to the distillation of the reaction liquid mixture, and thus the adhesion of the product to the wall by solidification during distillation can be prevented effectively.

[0008] The Grignard reagent of the present invention is prepared by using polyalkyleneglycoldialkylether expressed by the general formula [1] as the solvent. The polyalkyleneglycoldialkylether can be, for example, diethyleneglycoldiethylether, diethyleneglycoldibutylether, diethyleneglycolethylmethylether, dipropyleneglycoldimethylether, dipropyleneglycoldiethylether, dipropyleneglycoldibutylether, dipropyleneglycolisopropylmethylether, dipropyleneglycolisopropylethylether, triethyleneglycoldimethylether, tetraethyleneglycoldimethylether, tripropyleneglycoldimethylether, pentaethyleneglycoldimethylether, hexaethyleneglycoldimethylether, etc..

[0009] For the Grignard reagent expressed by the general formula [2] according to the present invention (R^4MgX), R^4 in the formula can be, for example, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, t-butyl group, n-amyl group, i-amyl group, hexyl group, octyl group, decyl group, dodecyl group, vinyl group, allyl group, 1-propenyl group, 1-methylvinyl group, 2-butenyl group, benzyl group, cyclopentyl group, cyclohexyl group, cyclooctyl group, 2-propynyl group, ethynyl group, phenyl group, o-tolyl group, p-tolyl group, 4-fluorophenyl group, xylyl group, etc., but it is not limited to these. Also, X in the formula can be, for example, a halogen atom such as chlorine atom, bromine atom, iodine atom, etc..

[0010]

[Examples] Now, the present invention is explained by examples.

[0011] Example 1

Magnesium 12.2 g (0.5 mole) and diethyleneglycoldiethylether 98 g were loaded in a flask of 500 ml furnished with a thermometer, a reflux condenser, a stirrer, and a dropping funnel, and n-propyl chloride 39.3 g (0.5 mole) was dropped while maintaining the liquid at 50 ~ 60°C in nitrogen atmosphere by taking 2 hours. After the completion of the dropping, the reactants were stirred at this temperature for 3 hours, and diethyleneglycoldiethylether solution of n-propylmagnesium chloride (Grignard reagent) was obtained. This Grignard reagent was analyzed quantitatively by Gilman method, and the yield of n-propylmagnesium chloride was 93 %.

[0012] Examples 2 ~ 9

By the same procedure as the example 1 by using various halides, Grignard reagent dissolved in polyalkyleneglycoldialkylether was obtained The results were summarized in Table 1.

[0013]

[Table 1]

example	halide	solvent in general formula [1]				usage	reaction	yield of Grignard
		R^1	R^2	R^3	n	(g)	temperature (°C)	reagent (%)
1	n-propyl chloride	Et	Et	H	2	98	50 ~ 60	93
2	n-butyl chloride	Me	Me	H	3	98	60 ~ 70	93
3	i-butyl chloride	Me	Me	Me	2	98	80 ~ 90	92
4	n-amyl chloride	i-Pr	Et	Me	2	106	50 ~ 60	93
5	n-hexyl chloride	Me	Me	H	4	98	50 ~ 60	94
6	n-octyl chloride	Bu	Bu	H	2	130	50 ~ 60	95
7	cyclopentyl chloride	Bu	Bu	H	2	130	50 ~ 60	87
8	cyclohexyl chloride	Bu	Bu	H	2	130	50 ~ 60	90
9	xylyl chloride	Bu	Bu	H	2	130	70 ~ 80	85

[0014] Example 10

Magnesium 12.2 g (0.5 mole), diethyleneglycoldibutylether 130 g, and toluene 50 g were loaded in a flask of 500 ml furnished with a thermometer, a reflux condenser, a stirrer, and a dropping funnel, and i-propyl chloride 39.3 g (0.5 mole) was dropped while maintaining the liquid at 40 ~ 50°C in nitrogen atmosphere by taking 2 hours After the completion of the dropping, the reactants were stirred at this temperature for 3 hours, and i-propylmagnesium chloride (Grignard reagent) was obtained. This Grignard reagent was analyzed quantitatively by Gilman method, and the yield of i-propylmagnesium chloride was 92 %.

[0015] Examples 11 ~ 19

By the same procedure as the example 11 by using various halides, Grignard reagent dissolved in polyalkyleneglycoldialkylether and hydrocarbon was obtained. The results were summarized in Table 2.

[0016]

[Table 2]

example	halide	solvent in general formula [1]				usage	hydrocarbon	reaction	yield
		R^1	R^2	R^3	n	(g)	solvent (g)	temperature (°C)	(%)
10	i-propyl chloride	Bu	Bu	H	2	130	50	40 ~ 50	92
11	t-butyl chloride	Et	Et	H	2	98	50	80 ~ 90	94
12	vinyl chloride	Bu	Bu	H	2	130	40	30 ~ 40	85
13	1-propenyl chloride	Bu	Bu	H	2	130	40	40 ~ 50	88
14	1-methylvinyl chloride	Bu	Bu	H	2	130	40	40 ~ 50	90
15	allyl chloride	Bu	Bu	H	2	130	32	5 ~ 10	82
16	2-butenyl chloride	Bu	Bu	H	2	130	32	5 ~ 10	80
17	phenyl chloride	Bu	Bu	H	2	130	50	70 ~ 80	88
18	benzyl chloride	Bu	Bu	H	2	130	50	5 ~ 10	74
19	2-propynyl chloride	Bu	Bu	H	2	130	50	5 ~ 10	68

[0017] Example 20

Diethyleneglycoldiethylether 20 g and toluene 30 g were loaded in a flask of 500 ml furnished with a thermometer, a reflux condenser, a stirrer, a dropping funnel, and a gas-blowing apparatus, and while acetylene gas 26 g (1.0 mole) was blown in, diethyleneglycoldiethylether solution of n-propylmagnesium chloride prepared in the example 1 (0.5 mole) was dropped from the dropping funnel at 20 ~ 30°C in nitrogen atmosphere by taking 2 hours. After the completion of the dropping, the reactants were stirred at this temperature for 1 hour This Grignard reagent was analyzed quantitatively by Gilman method, and the yield of the Grignard reagent was 91 %

[0018]

[Effect of the invention] As is clear from the results of the examples 1 ~ 20, Grignard reagent can be prepared in high yield by using a specific polyalkyleneglycoldialkylether as the solvent. When this Grignard reagent dissolved in polyalkyleneglycoldialkylether is used, magnesium halide complex generated as the by-product of coupling reaction between the Grignard reagent and the other compound is dissolved, and thus even in the case the product tends to be hydrolyzed by water, it can be separated and purified easily by distillation, etc. without after-treatment with water.

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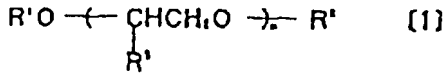
(54)【発明の名称】　グリニャール試薬

(57)【要約】
【構成】一般式〔１〕
【化１】



〔１〕

（R^1、R^2：炭素数１～８のアルキル基、R^3：水素原子又はメチル基、ｎ：１～６の整数）で表わされるポリアルキレングリコールジアルキルエーテルを溶媒とするグリニャール試薬。
【効果】本発明のポリアルキレングリコールジアルキルエーテルを溶媒とするグリニャール試薬を用いれば、グリニャール試薬と他の化合物とのカップリング反応で副生するハロゲン化マグネシウム錯体が溶解され、生成物が水で加水分解し易い場合でも、水で後処理することなく生成物を蒸留等によって簡易に分離・精製することが可能となる。